

PCT

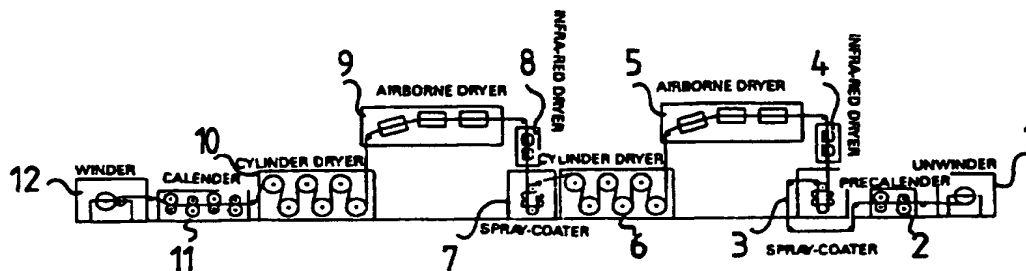
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : D21H 23/50	A1	(11) International Publication Number: WO 97/13035 (43) International Publication Date: 10 April 1997 (10.04.97)
(21) International Application Number: PCT/FI96/00525 (22) International Filing Date: 7 October 1996 (07.10.96) (30) Priority Data: 954745 5 October 1995 (05.10.95) FI (71) Applicant (for all designated States except US): VALMET CORPORATION [FI/FI]; Panuntie 6, FIN-00620 Helsinki (FI). (72) Inventors; and (75) Inventors/Applicants (for US only): KOSKINEN, Jukka [FI/FI]; Vehkatie 89, FIN-04400 Järvenpää (FI). KIRVESKARI, Erkki [FI/FI]; Valihaka 90, FIN-07190 Halkia (FI). NISSINEN, Vilho [FI/FI]; Onkimaantie 195, FIN-04660 Numminen (FI). KINNUNEN, Jorma [FI/FI]; Johan Sederholmintie 2 B 22, FIN-00810 Helsinki (FI). LUOMI, Seppo [FI/FI]; Purukuja 2 A, FIN-04440 Järvenpää (FI). (74) Agents: LAINÉ, Seppo et al.; Seppo Laine Oy, Lönnrotinkatu 19 A, FIN-00120 Helsinki (FI).		(81) Designated States: AU, BR, CA, JP, KR, US. European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>In English translation (filed in Finnish).</i>

(54) Title: **METHOD AND APPARATUS FOR COATING A MOVING PAPER OR CARDBOARD WEB**



(57) Abstract

The invention relates to a method of coating a moving web of paper or paperboard. In the method, the web to be coated is passed to a coater station, wherein a coat layer is applied to at least one surface of the web, and the web is dried at least to some degree and passed to the next treatment step. The coat is applied by spraying the coating mix on the web surface by means of high-pressure spraying nozzles, whereby the pattern width covered by a single nozzle is essentially narrower than the cross-machine width of the web being coated.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

Method and apparatus for coating a moving paper or cardboard web

5 The present invention aims to provide a method according to the preamble of claim 1 for coating a moving web of paper or paperboard in a manner permitting applicator or levelling apparatuses to operate noncontactingly on the web.

10 The invention also aims to provide an arrangement suited for implementing said method, that is, an applicator apparatus in which the coat is applied to the web in a noncontacting fashion directly as a coat layer of desired thickness.

15 To improve the printability of paper, the paper may be coated with a coating formulation containing mineral pigment and binder components. Over the years, application and levelling of the coat have been carried
20 out using a variety of apparatuses. Higher web speeds and increased demands on process efficiency and paper quality in combination constitute the stimulus driving the development of applicator equipment.

25 Initially, paper coating with a pigment-containing formulation was performed using coaters of the gate roll type, in which the coating mix was first metered with the help of furnish rolls to a set of transfer rolls, and there-
30 from further to the moving web of paper. However, the function of such a coater is impaired at web speeds exceeding 400 m/min. The nips of the rolls start to throw out splashes of the coating mix, and the coating process lacks the stability required to achieve an acceptable coat quality. Furthermore, well-behaved control of coat
35 weight is difficult to achieve when using the above-described technique.

Particularly for surface sizing, sizing presses have been used in which the downward running web is passed through a coat mix pond sealed by the rolls. Herein, a problem arises from the strong increase of moisture content in the web and difficult controllability of the correct amount of applied size.

In the kiss-coating technique, the coating mix is metered directly in a nip from the casting roll to the surface of the paper web. In the early days, and in paperboard coating even today, excess coat is doctored away with the help of an air knife. At web speeds above 500 m/min, however, the impact force of the air flow from the slot orifice of the air knife is insufficient for effective doctoring of the coat layer applied to the web surface.

An essential increase in coating speed was facilitated by the adoption of the doctor blade levelling technique for controlling the final coat weight. In the first generation of blade coaters, the web was arranged to run from above downward and the coating mix was pumped into a pond formed in the recess between the backing roll and the blade. In fact, the same technique is still being used in two-sided coating.

The actual break-through of the blade coating technique occurred along with the adoption of the transfer coating method. Herein, the coat is applied directly to the web surface in the nip between a transfer roll and a backing roll. Excess coat is removed by means of a doctor blade extending over the entire web width. This kind of coating technique makes it possible to increase the web speed to about 1300 m/min. At web speeds above this, splashing of the coat at the nip and the air film which is entrained in the nip along with the moving web, thereby causing skip marks on the coated web, make the use of this method extremely complicated if not impossible. The higher the

web speed, the fewer degrees of freedom will be available in the selection of coat mix components. Herein, the coating mix formulations must be selected under the constraints of web runnability, sometimes even compromising the quality of the end product.

Due to the poor runnability of transfer coaters, a short-dwell doctor blade coater was developed to provide an alternative technique for applying light coats to thin-caliper paper grades. In this type of coater, the web is guided past a slot orifice box which is formed by a short-dwell application chamber and the doctor blade and is adapted to operate against a backing roll. This method has been extremely popular in the art and facilitated effective on-machine coating. Also in this method, the maximum practicable web speed has turned out to be the limiting factor for further development. At web speeds above 1300 m/min, striping will appear at coat weights higher than 9 g/m² due to turbulence in the applicator flow chamber. In addition, an essential impairment of the cross-machine coat profile occurs with higher coat weights.

Improvements in the design of film transfer-type coaters typically used in surface sizing of paper have extended the use of these coaters to the application of pigment coats, too. Herein, the coating mix is first metered by means of an apparatus similar to a short-dwell coater onto a transfer roll, wherefrom the coat film is further transferred in a nip of two rolls to the surface of the paper web. This novel technique was initially introduced to surface sizing and later also to the application of a pigment coat at unconventionally high web speeds. However, problems are encountered in the form of coat mist and splashing occurring at the splitting point of the coat film when the web exits the film transfer nip. When applied at high web speeds, coats heavier than 10 g/m²

suffer from an orange-peel texture and other low-quality surface properties incapable of fulfilling all the specifications that are set on a finished end product.

5 The coat splashing and web skipping problems occurring on the application roll have generally been overcome by means of the nozzle application technique, which gives a wider latitude in the direction of higher web speeds. Additionally, better capabilities of applying heavy coat
10 weights have been attained through more effective water drainage offered by the longer dwell time. Moreover, the coat forms close to the base sheet surface a layer of higher solids content that provides support to the doctor blade, whereby blade stability is improved and cross-
15 machine profiles of improved evenness are attained.

When the nozzle-application step based on a doctor blade and a subsequent levelling step based on a scraper element are performed against the same backing element, a
20 runnability complication in the form creases and/or bags in the web generally occurs. This problem can be eliminated by implementing the application and levelling steps against separate backing elements. Due to the resultant increase of dwell time and paper moisture content, some
25 difficulties will be encountered in the runnability of lightweight and high-moisture-absorbance paper grades.

The striping problem of short-dwell coaters has been alleviated with the dam blade construction known from the
30 film transfer method of coating. However, all the above-described application methods are hampered by the mechanical contact and load imposed on the web by the coater. Particularly in blad coaters, paper production will easily be disrupted by defects in the base sheet. Paper
35 mills have a strong drive to improve the efficiency of coater lines. Obviously, valuable production time will be lost due to web breaks. In conventional application

techniques, the time to regain an acceptable quality after a web break takes an unduly long time.

For wet-on-wet coating, a blade coater is not necessarily
5 the best possible alternative. In this coating method, to the same side of the web are applied at least two coat layers so that onto the first coat, while still moist, is directly applied the next coat layer without intermediate drying. Particularly in the application of a precoat, web
10 defects like striping and unevenness are extremely detrimental. Therefore, a blade coater requires continuous control to keep the coat weight at its set value. Hence, a facility for measuring the precoat weight is mandatory in order to maintain controlled coat application. Such a
15 coat weight measurement system operating between the successive application steps of coat layers is expensive and sometimes even impossible to arrange. Therefore, stable operation is required from wet-on-wet coaters so that the application and levelling of subsequent coat
20 layers can be carried out without spoiling the already applied, still moist coat layers.

Attempts have been made to improve runnability in paper machines and coating stations with the help of supported
25 web threading. Herein, an extremely smooth surface is required from the support wires or belts used in coaters. Furthermore, even the smallest irregularities of backing surfaces will cause coat marking not only particularly in blade coaters, but also in transfer coaters.

30 At higher web speeds, the rate of successfully performed flying splicing on the unwinder of off-machine coaters falls significantly. Splicing apparatuses required herein become expensive, and nevertheless problems will occur in
35 exact timing of splicing. Therefore, future development of coaters must aim to provide an on-machine coater embodiment in which such problems associated with

splicing and roll change cannot disturb the finishing treatment.

5 A blade performing the doctoring of the coat applied to the web tends to accumulate aggregations of dirt under the blade edge that cause striping of the coat. Due to such coating defects, large amounts of finished paper turn into scrap.

10 The rheological properties of the coating mix may cause web runnability problems due to the extremely strong fields of high shear rate acting on the coat mix in the blade tip region. Accordingly, the selection of possible coating mix formulations is often curtailed by the rheological constraints associated with the blade geometry.

20 In order to overcome the above-described drawbacks, paper coating should preferably be carried out using a noncontacting method. Through the use of a noncontacting method for coating the web, defects of the base sheet are prevented from disturbing the finishing treatment. Complemented with a web threading system which is fully supported by wires and belts, it is possible to achieve a break-free, even a fully automated coating process.

25 Herein, paper web defects can be identified by means of defect detectors and removed during intermediate winding in order to prevent them from interfering with further processing. Development of equipment for higher web speeds is no more hampered by load imposed on the web.

30 The opacifying power of the applied coat becomes so good that the air knives, which today are the major factor limiting the maximum speed of paperboard coaters, can be replaced by the novel technique. Thus, the efficiency of coating lines and production throughput of coaters can be elevated to a remarkably high level.

Noncontacting coating methods are mentioned in, e.g., patent applications PCT/US91/03830, FI 925404 and FI 933323. In the coaters discussed therein, the coating mix is fed into the nozzle via a separate duct, and atom-
5 ization of coating mix is performed with the help of compressed air passed to the nozzle. However, tests to be described in greater detail later in the text have shown that insufficient atomization results from the use of a nozzle based on blast-diffusion by compressed air. Mor -
10 over, such a strong airflow causes excessive evaporative drying of the coating mix droplets before they can impinge on the sheet surface. Droplets of excessive size in the coat mist make the finished surface pitted and unsmoothly coated, which is manifested in the coat
15 profile as craters and mounds.

Patent applications FI 911390, US 248,177 and PCT/FI89/00177 discuss applicator apparatuses in which the coating mix aerosol is formed in a separate chamber
20 or apparatus using a gas-liquid nozzle or ultrasonic diffusor nozzle. The coat aerosol is passed into an applicator nozzle, wherein the aerosol is directed by means of separate gas injection to impinge on the sheet surface. The portion of the coating mix aerosol not
25 adhering to the web is returned by suction back into the coating mix circulation. In such an apparatus, the coating mix droplets undergo evaporation before reaching the sheet surface, whereby their adherence to the sheet is impaired. Subsequently, when the paper is used in a
30 printing shop, a large amount of dirt will build on the printing machine rolls and the coat will release dust in the trimming and folding equipment.

In the apparatus described in the patent application
35 PCT/FI93/00453, the coat is applied using the above-described methods and then levelled using a doctor unit. This method represents a kind of direct application with

th exception of its conventional doctor blade technique, whose shortcomings were described above.

Noncontacting coater equipment are well-known and frequently used apparatuses in the art of painting and coating systems technology. High-pressure spraying equipment with suitable nozzles are commercially available for painting. However, the use of high-pressure spraying for applying coating mix to a moving web of paper or paper-board in the fashion described in detail later is a novel application of the noncontacting application technique.

In order to make it possible to spray a coating mix or material onto a surface to be coated, the fluid material must be dispersed into small droplets. This step is called atomization. The basic idea of atomization covers a variety of different uses ranging from painting to varied combustion installations, engines and apparatuses for mass and heat transfer such as gas scrubbers and evaporation towers. As a general term, atomization refers to conversion of fluid material into droplet form (that is, particles of round or similar form). The type of the spray is categorized according to the cross-sectional shape of the spray jet. Normally, a hollow or solid conical or fanned spray is used. Spray coverage is defined as the width of the spray pattern at a certain distance from the nozzle tip. The spray angle is the opening angle of the spray cone emitted by the nozzle.

Atomization nozzles fall into four different classes:

- 1) High-pressure airless nozzles (pressure atomizers)
- 2) Atomizers based on rotary centrifugal atomization (rotary atomizers)
- 3) Air-assist and air-blast nozzles (twin-fluid atomizers)
- 4) Other methods.

High-pressure atomizers are characterized in that ther in atomization occurs driven alone by the internal pressure of the fluid being atomized. No atomizing air is used. In practical tests, airless atomizing nozzles have been
5 found superior to air-blast nozzles.

In pilot-scale tests of the present invention, the spraying technique was first adapted to the application step of the coating mix. Levelling of the applied coat was
10 performed using conventional doctor blade techniques. However, this combination did not offer any benefit over prior-art nozzle application methods.

Following shortcomings were found in this method:

- 15
- for the nozzle types used in the test, the viscosity of the coating mix was too high to permit sufficient atomization of the coating mix so that a smooth coat could be applied;
 - 20 - coating mix droplets did not gain sufficient kinetic energy to adhere and spread sufficiently on the sheet surface; and
 - pressure levels used in the fluid atomizing nozzles were insufficient for the atomization of the coating mix.

25

Coating mix used in the atomization application method must have a sufficiently high kinetic energy to drive the coat droplets formed at the nozzle home against the sheet surface so as to flatten and adhere the droplets to the web surface. At higher web speeds, the droplets must also
30 be capable of penetrating the barrier formed by the air film travelling along with the moving sheet surface. These requirements cannot be fulfilled by means of an air-blast atomizing nozzle. This is because the blasting
35 air flow causes strong evaporation of the coat droplets, whereby the deposition and spreading of the coating mix

droplets on the sheet surface is worsened. Hence, the achievable coat quality remains unsatisfactory.

5 It is an object of the present invention to provide a noncontacting method of coat application free from the shortcomings of the above-described techniques.

10 The goal of the invention is achieved by means of performing the coat spraying step onto the sheet surface with the help of high-pressure nozzles.

15 More specifically, the method according to the invention is characterized by what is stated in the characterizing part of claim 1.

Furthermore, the arrangement according to the invention is characterized by what is stated in the characterizing part of claim 12.

20 The invention offers significant benefits.

The present method of entirely noncontacting coat application, which is free from any need for coat doctoring, is capable of significantly improving the runnability of coating equipment. The method applies no strong forces loading the web, whereby coating may be carried out against a web running over a backing roll, belt or even unsupported. High-pressure airless spraying nozzles give an extremely smooth surface, which has a coat profile similar to that obtained by means of an air knife, however, with a smoother profile, in some cases even smoother than that of a doctored coat. Obviously, the smoothness of the coated web is affected by the base sheet profile, and therefore, the base sheet to be coated is advantageously run through a precalendering step prior to the application of the sprayed coat. In the method, the coat settles as a uniform layer of constant thickness

on the base sheet surface, whereby a high opacifying power of the coat layer is attained. Hence, the method is particularly suited for coating only semibleached paper-board grades. The control of coat weight and profile is
5 easy by way of altering the number of nozzles and coat pumping rate to each individual nozzle. On the basis of tests performed, it appears that the impact of the coat spray on the sheet does not cause strong migration of water from the coating mix into the base sheet. The
10 method is extremely well suited for wet-on-wet coating, because the coat sprays emitted by the nozzles do not agitate the previously applied layer and the load imposed on the moist web remains low.

15 In the following, the invention will be examined in greater detail by making reference to the appended drawings in which

Figure 1 shows a first coating line configuration implemented according to the invention;
20

Figure 2 shows a second coating line configuration implemented according to the invention;

25 Figure 3 shows a third coating line configuration implemented according to the invention;

Figure 4 shows a fourth coating line configuration implemented according to the invention;
30

Figure 5 shows a fifth coating line configuration implemented according to the invention;

35 Figure 6 shows a sixth coating line configuration implemented according to the invention;

Figure 7 shows a seventh coating line configuration implemented according to the invention;

5 Figure 8 shows an eighth coating line configuration implemented according to the invention;

Figure 9 shows a ninth coating line configuration implemented according to the invention;

10 Figure 10 shows a tenth coating line configuration implemented according to the invention;

Figure 11 shows an eleventh coating line configuration implemented according to the invention;

15 Figure 12 shows a twelfth coating line configuration implemented according to the invention;

20 Figure 13 shows a coater unit according to the invention having three applicator assemblies mounted about a single backing roll; and

25 Figure 14 shows a coater unit according to the invention having four applicator assemblies mounted about a single backing roll.

According to the invention, the coat is applied to a web 1 by means of high-pressure airless spraying nozzles. The fluid coating mix is atomized in the nozzle heads by
30 passing the pressurized liquid through a small-orifice nozzle. Thence, the core component of the spray-coater apparatus is the coat-atomizing nozzle. Test results indicate that high-pressure spraying nozzles of the airless type are generally to be preferred. The fluid may be
35 pressurized in the range of 1 - 1000 bar. However, pressures typical in the art vary in the range 100 - 300 bar. It has been found that pressures under 100 bar can under

no conditions atomize the coating mix into droplets of sufficiently small size.

Typically, the spray-coater apparatus includes a nozzle assembly incorporating nozzles designed to emit fan-shaped sprays. The main axes of the fanned spray patterns of the nozzles are rotated by approx. 7 - 15° with respect to the cross-machine main axis of the nozzle set, whereby a relatively smooth coat profile results. The nozzle assembly is also characterized by an adjustment facility of the internozzle distance and the distance of the entire nozzle assembly from the base sheet. The most uncomplicated design of the nozzle adjustment is such that offers a simultaneous adjustment for all the nozzles of the system and provides as identical conditions as possible for all the nozzles. Obviously, a separate adjustment for each nozzle would give certain latitude for the coat profile control over the cross-machine width of the nozzle spray pattern. Additionally, individual control of the nozzles could be used to some extent for compensation of orifice wear in the nozzles.

On the basis of tests performed, it has been found that the effective practicable spray pattern width achievable by means of a single nozzle is about 10 to 30 cm. This means that from 10 to 3 nozzles, respectively, are required per linear meter of web width. As it is plausible that a uniform coat quality cannot be attained by means of a single linear array extending over the entire web width, the spray-coater apparatus advantageously comprises a plurality of linear nozzle arrays.

Formation of coat mist is one of the problems of the spray-coating method needing an effective solution. Elimination of coat mist formation can be categorized into four tasks: 1) the conditions of coating mix spraying are made such that the deposition of spray d

particles on the web occurs as unobstructed as possible, which in practice means removal of the air film travelling along with the surface of the moving web; 2) such nozzle designs are selected that produce droplets of as uniform size as possible, whereby the number of droplets of small size and kinetic energy is minimized; 3) the adhesion of the coat droplets to the web is maximized by all means, whereby such operating parameters as the electrostatic charging of the droplets, coating mix formulations and appropriate impact force of the fluid droplets on the web must be evaluated; and 4) suitable mechanical mist collector systems are used.

The spraying-nozzle unit must be located so that it can be sealed sufficiently tightly against a suitable backing surface. Such surfaces are offered at least by a web-supporting roll, belt, felt or wire. In this context, the term sealing refers to the sealing of the peripheral areas of the applicator unit and of the edge areas of the web as well as controlled travel of the web at the ingoing and outgoing ports of the spray-coater. Such sealing is extremely crucial for proper collection of the stray coat mist.

Spray-coating requires efficient removal of the air film travelling along with the web. The air film forms a barrier to the deposition of the sprayed particles on the web. As the removal of the air film also helps to reduce the formation of coat mist, the air film should be removed as effectively as possible and as close as possible to the ingoing port of the spray-coater unit. The removal of the air film from the web surface can be accomplished by means of an arrangement operated in a doctor blade fashion, or alternatively, by adapting an air knife to blow against the web travel direction. By contrast, removal of the air film from the web surface inside the spray-coater unit may become a complicated task, because

the coat mist tends to deposit on any surface inside the spray-coater unit.

5 Doctoring-away of the air film is an important step to be carried out just before the ingoing side of the spray-coating assembly. Such a doctoring of the air film can be implemented by means of, e.g., counterblowing based on air injection from an air knife reverse to the web travel direction. Also various doctor blade arrangements are
10 suitable for the removal of the air film. The optimum location for such an air-layer-doctoring accessory is in the immediate vicinity of the spray-coater ingoing side. While the accessory elements may also be located inside the housing of the spray-coater unit, such a placement
15 necessitates additional clean-keeping arrangements.

The coating mix must be furnished into the coating mix machine tank of the coater separately for each coating run with a specific formulation suited for spray-coating.
20 The replenishment of fresh coating mix into the machine tank can be arranged to occur continuously or batch-wise. An essential requirement herein is that the coating mix must have a homogeneous composition with suitable physical properties. The constituents of the desirable coating
25 mix formulation are determined separately for each base sheet type and grade. The viscosity and solids content of the coating mix are adjusted compatible with the spray-coating method. Generally, coating mix formulations optimized for spray-coating have a low solids content and
30 viscosity as compared to coating mixes used in doctor blade coater.

In the following, examples are given of various coating line arrangements using spray-coater units for coat
35 application. The spray-coater units themselves are described in a co-pending application based on the FI Pat. Appl. No. 954,745.

Shown in Fig. 1 is a simple off-machine coating line adapted for single-layer, two-sided coating of paper web. The first unit of the line is an unwinder 1, after which the web is taken to a precalender 2 comprised of, e.g., a nip of two soft rolls and one hard roll. Next after the precalender 2 is a spray-coater unit 3 in which a desired coat layer is applied to the first side of the web. The actual coater unit comprises a belt-backed coater in which the coat is applied in two steps to the web supported by the belt. Such a coater unit is capable of applying a heavy coat in a single pass. Subsequent to coating, the web is threaded to an infra-red dryer 4, followed by drying on an airborne dryer 5 and finally on a cylinder dryer 6. Immediately after drying, the dried web is passed to a second spray-coater unit 7, followed by another sequence of the above-described equipment comprising drying on an infra-red dryer 8, airborne dryer 9 and cylinder dryer 10. Subsequent to drying, the paper web is recalendered on a machine calender 11 comprising four nips and rewound into rolls on a winder. The coating line of Fig. 2 differs from the above-described system in that the winder is adapted immediately after the second coater and dryer section. The line is complemented with separate calenders, a soft-nip calender 13 and a supercalender 14.

One of the benefits of the coating lines shown in Figs. 1 and 2 is their simple structure which, however, with the help of pre- and postcalendering is capable of providing a very smooth coat combined with the extremely good opacifying power of spray-coating. Additionally, the equipment of Fig. 2 can be readily modified for making paper grades of different finishes by varying the coating mix formulation and the degree of calendering. The coating lines of Figs. 3 and 4 are equivalent to those described above with the exception that they are directly connected to a paper machine 15.

In Fig. 5 is shown a paper machine 15 directly followed by a coating line for two-sided coating of a paper web. The web exiting the paper machine 15 is first taken to a precalender 2, followed by a spray-coater station 16, which in the illustrated configuration comprises three spray-coater units, all of them being adapted to apply the coat to a web passed over a backing roll. After the application of the first coat layer, the web is dried in the above-described fashion, and subsequently the other side of the web is coated on a backing-roll-type coater station 17, then dried and finally passed to an intermediate calender 18. Intermediate calendering is followed by the application of a second coat layer first to the first side of the web on a coater station 19, followed by a drying sequence comprised of an infra-red dryer 20, an airborne dryer 21 and cylinder dryers. The other side of the web is coated on the coater station 23 and dried on dryers 24, 25, 26, followed by the calendering 27 and winding 28 steps. Owing to the improved runnability of the spray-coater line over all conventional coating methods, the method is highly suited to on-machine coating. The configuration shown in Fig. 5 produces extremely smooth paper, since the precalendered and already spray-coated paper as such has a relatively smooth surface, which is further smoothed by intermediate calendering. Thence, the coat layer applied in the second stage is sprayed onto a smooth paper surface, thereby improving its smoothness prior to final calendering, which still more enhances the coat smoothness. Further, the double-layer coating can be made using different kinds of coats, whereby the whiteness and other properties of the finished sheet can be made extremely good.

The configuration of Fig. 6 is an off-machine coating line for two-sided coating of paper web. Therein the coater stations are belt-backed spray-coater stations 3, 7, 29, 30, which can be used to apply a large amount of

coat. Drying herein is performed analogously to the above-described examples with infra-red, airborne and cylinder dryers. While the intermediate calendering stage between the application of the first and second coat layers is omitted, the configuration is complemented with a separate soft-nip calender 13 and a supercalender 14. Thence, the different calendering methods can be used so as to affect the surface gloss of the finished sheet making the configuration of Fig. 6 suitable for manufacturing paper grades optimized for different printing purposes through varying the formulation of coating mixes and the method of calendering.

In Fig. 7 is shown a double-layer coating configuration in which the first coat layer is applied by the spray-coating method and the second layer by a blade coater. Paper finishing starts from an unwinder 1, followed by a precalendering stage 2 and application of the first coat layer on a belt-backed spray-coater station 3. Drying is carried out analogously to the preceding examples. The other side of the web is coated and dried in the above fashion, followed by blade coating on both sides of the web. In the illustrated example, the blade coating is carried out on kiss-coater stations 31 and 32. The coat applied by the casting rolls is dried in the same fashion as the sprayed coats, but the web is herein threaded slightly differently due to the modified structure of the coater station 31, 32. After two-sided coating and drying of the web, the web is taken to the winder and calendered if necessary on separate soft-nip and supercalenders 13, 14. In this coater configuration, the paper surface can be finished to the coat smoothness characteristic of blade coating, whereby the sheet surface quality becomes slightly different from that offered by spray-coating alone. Further, since blade coating can use coat formulations different from those of spray-coating, it is herein possible to use blade coating in the case that the coat-

ing mix desirably used in the top coat is not suitable for spray-coating due to, e.g., its high viscosity. Also this arrangement provides an extremely high surface quality, because it combines the good opacifying power of spray-coating with the smooth profile and high surface quality of blade-coated sheet.

In Fig. 8 is described a coating line configuration in which the order of the spray-coater and blade coater sections are interposed. In this coating line, the first coater section using a doctor-blade apparatus applies to the sheet surface a coat layer capable of filling the pores of the web, whereby the web surface is smoothed so that also the sprayed coat applied next to this smooth surface also gives a smooth final coat profile. However, as the coat profile obtained by spray-coating is not as planar as a doctored surface, the final coat quality is slightly different from that obtained by the coating line configuration of Fig. 7. Owing to spray-coating, extremely good opacifying power is obtained in both configurations.

In the coating configuration of Fig. 9, the spray-coater section is combined with a film transfer coater section. Herein, film transfer coating is carried out as the first application stage in the same fashion as in most prior-art coater arrangements. Since the film transfer coating method imposes minimal stress on the web and is highly reliable, the coating line of Fig. 9 can provide extremely good runnability combined with low load on the web. Also in this configuration the web is passed immediately after the unwinder 1 to a precalender 2, followed by the application of the first coat layer on a film transfer coater 35. The other side of the web is treated similarly by the next film transfer coater 36, followed by drying in the same fashion as the preceding examples. After both sides of the web are treated, the web is passed to an

intermediate calender 18, followed by coating on spray-coaters 29, 30 and winding up. When necessary, finishing calendering can be made on a separate soft-nip calender 13 or a supercalender 14. The principal benefit of this configuration is the good opacifying power of the applied coat combined with good runnability. Particularly by virtue of the excellent runnability, the illustrated configuration can be used for coating the most lightweight base sheets.

The configuration of Fig. 10 is otherwise equivalent to that described above with the exception that the film transfer coaters used for applying the first coat layer are replaced by blade coaters 33, 34. Hence, this configuration is similar to that of Fig. 8 with the exception of the intermediate calender 18. Owing to such intermediate calendering, this configuration makes it possible to manufacture even smoother paper than that provided by the configuration of Fig. 8.

Figs. 11 and 12 illustrate configurations which feature superior runnability over conventional coating lines. In both examples, coating and drying takes place noncontactingly. In the configuration of Fig. 11, the unwinder 1 is immediately followed by a precalender, wherefrom the web is passed to a belt-backed spray-coater 3. From the coater 3 the web is passed straight without essentially deflecting its direction to an infra-red dryer 4 and therefrom to an airborne dryer 5. After drying, the other side of the web is coated and dried in a similar fashion, followed by the application and drying of the second coat layer. The web is threaded substantially straight over its path through the two application stages and is only contacted by the support belts of the spray-coater stations 3, 7, 29, 30.

After double-layer coating of the web, the web is deflected by guide rolls 37 to run upward and backward for a second double-layer coating sequence on belt-backed spray-coaters 38, 39, 40, 41. This sequence of the third and fourth coating steps with their drying steps is carried out in a similar fashion to those of the two preceding coating steps, and finally the web is passed to a winder 12. When necessary, finishing calendering can be made by a separate soft-nip calender 13 or a super-calender 14.

The configuration of Fig. 12 is otherwise similar to that of Fig. 11 with the exception that all coating steps are carried out on a single coating line. The benefit of this configuration is the entirely linear path of the web, however, involving the penalty of long footprint in the machine direction.

By virtue of the configurations of Figs. 11 and 12, the advantages of noncontacting spray-coating can be maximally benefitted as the web is passed through the entire coating line almost without any mechanical support. Furthermore, no load is imposed on the web during coating or drying. Advantage is also taken from the cost-efficient structure and small dimensions of spray-coaters which can readily be adapted to a rather wide spectrum of paper treatment tasks. As the spray-coating method is capable of applying extremely thin coats, too, multilayer application up to four passes can be performed economically in order to achieve a certain type of coat, even when the overall coat thickness must be relatively small. Obviously, the same coating method is capable of applying thick coats, too. Hence, this type of multilayer coating opens new possibilities of manufacturing improved paper grades that can be better tailored for a specific use. The coating line is extremely adaptable offering fast change of paper grade, whereby smaller lots can be

flexibly manufactured according to customer needs and market demand.

5 Since the spray-coating method according to the invention does not agitate the previously applied coat layers, the above-described exemplifying embodiments of coating lines can be configured into wet-on-wet coating lines if the number of dryers is desirably reduced due to lack of installation space or need for bargaining the equipment price. Herein, one of significant benefits of the invention is utilized, namely, that the web need not necessarily be dried entirely after one application step before the next application step.

15 Figs. 13 and 14 show two exemplifying embodiments of spray-coater units. The coater unit of Fig. 14 comprises a backing roll 45 and four applicator assemblies 42, each including three parallel linear nozzle arrays 43. In this fashion, a sequence of four successive coat layer applications can be adapted into a single coater unit. The coater unit of Fig. 15 has three applicator assemblies. The sole purpose of these illustrations is to bring forth a practicable structure of the spray-coater unit according to the invention and to elucidate the minimal space need of such a coater. Owing to their simple structure and minimal space requirement, the coater units can be located in almost any position in the coating line, even inside a paper machine, whereby these coaters make it possible to implement a wide variety of coating lines as outlined above. Different constructions of spray-coater units are described in greater detail in a co-pending patent application based on the same priority application as the present patent application.

35 The method according to the invention has been applied in coating tests with results discussed below.

Coating of a full-width web in the tests was generally successful, even to an unexpectedly good degree. Three adjacent spraying zones did not provide a sufficient capacity for attaining high web speeds. The coating capacity was approx. 10 g/m² at 220 m/min web speed and approx. 5 g/m² at 470 m/min. The solids content of the coating mix was 40 %. This test did not aim at determining the maximum performance values of the method.

Spray-coating is hampered by strong dusting of the spraying point environment by coating mix particles. The atomized spray of small coating mix droplets can spread everywhere along with air streams unless collected away in a controlled manner. Additionally, the air film travelling with the moving web surface tends to drag along the dust. In the test runs, a blade made from polyacrylate sheet was used for doctoring the air film away.

The kinetic energy imparted to the sprayed droplets must be sufficiently high, particularly at high web speeds, in order to prevent the moving air film from entraining the coating mix spray even before the spray can impinge on the web surface.

In the test run, the capacity of the nozzles per unit time was measured. When the amount of coating mix adhering to the web is known, also the portion lost in the environment can be calculated. Adjustment of suction fan capacity was found to affect the applied coat weight to a significant degree. The stronger the suction, the less coat could be deposited on the web surface.

The capacity of the nozzles was measured for two different types of nozzles. Nozzle code FF-610 indicates a nozzle with 60° spray angle and 0.010" (0.254 mm) nozzle orifice diameter. The other nozzle tested was with the same spray angle but with 0.012" (0.305 mm) orifice.

The actual tests were performed on the FF-610 nozzle at 160 bar pressure, whereby the nozzle output was 7.5 g/s of wet coating mix. The coating efficiencies (portion of coating mix adhered to the web from the overall amount of sprayed coating mix) at different web speeds are calculated in Table 1.

Table 1. Coating efficiency vs. web speed.

Test point	Av. coat weight over 1 m unit width of web [g/m ²]	Web speed [m/min]	Coating efficiency [%]
218	10.0	220	87
221	5.0	470	93
223	7.5	280	83
229	5.0	449	89

As can be seen, the coating efficiency varied in the range 83 - 93 %. On the average, the loss of sprayed coating mix was 12 %.

The webs were measured for cross-machine profiles of base weight, ash and caliper. To speed the measurement, all five profiles were printed sequentially into the same profile plot.

The measurement results shown that the fan-shaped spray pattern of the individual nozzles remains very clearly detectable and the coat weight profile is peaked. Profile deviation from nominal coat weight can be as much as about 6 g/m² per side. A peak is seen in the coat weight profile at the intersection of the fan edges. Examination of the coat profiles gives a peak-to-peak deviation of 40 - 60 % from the overall coat weight. An interesting

observation is, however, that the profile errors are not particularly visible on the finished product, which tells of the good opacifying power of the coat. The edge areas of the sprays can be blended smoother by making the spray angle of the nozzles wider, and the greater number of spraying zones required at higher web speeds will finally reduce the fan intersection errors to an insignificant level. Low web speeds necessitate the use of lower-output nozzles to prevent the errors of a single application zone from becoming excessively pronounced. When arranged into a three-row array, the nozzles tested herein are sufficient for applying a coat weight of 10 g/m^2 at 220 m/min web speed. To apply the same coat weight at a web speed of 440 m/min, the spray-coater would require a 6-row nozzle assembly, for a web speed of 880 m/min a 12-row assembly and so forth. Then, the profile error caused by a single nozzle will be reduced respectively.

While the coat profiles of a paper passed through a SymSizer size press are peak-free, a certain amount of skew toward the drive side can be seen. A pronounced valley occurs in the coat weight profile very close to the drive-side edge.

Prior to the tests, the greatest doubts were expressed with regard to the surface strength of the sprayed coat. Intuitively, the coat mist was expected to settle in the same fashion as snowflakes on the sheet surface. However, no differences could be found in the coat surface strength in contrast to paper passed through a SymSizer size press. Also the rolls of the supercalender and the printing machine remained free from buildup of coat dirt. Additionally, such a high coat surface strength indicated that the coating mix does not undergo phase separation when exiting the nozzle.

The coated paper was supercalendered to test runnability of spray-coated paper on a full-scale supercalender and to compare its behavior with that of supercalendered paper passed through a SymSizer size press. The spray-coated paper grades were found uncomplicated to run on a calender. The calender rolls remained free from buildup of coat dirt.

The spray-coated paper grades were readily printable. On the basis of samples returned from the printing shop, the following observation could be made:

- spray-coating is a viable application method for coating a web;
- buildup of coat dirt on the rolls of printing machines using spray-coated paper remains insignificant;
- a pronounced difference is seen between the surfaces of transfer-coated and spray-coated paper grades that becomes more accentuated at higher coat weights;
- spray-coating gives a smoother visual appearance, but not as good a printed surface gloss and density as that offered by a transfer-coated paper;
- orange-peel texture is more pronounced on a transfer coated sheet;
- supercalendering of the base sheet clearly improves the surface quality of spray-coated paper.

Overall results of web coating by spraying techniques widely surpassed the expectations laid on the method. Paper surface strength in calendering and printing is imperative prerequisite for further development of the method. At least on the basis of tests performed, sufficient strength of coat surface seems to be attainable.

As compared visually to a comparative sample passed through a SymSizer size press, the paper surface and printing quality seemed smooth, even promising. Under

visual examination, the print gloss and density of spray-coated paper did not reach the quality level of the comparative sample.

5 The paper surface appears well-opacified and no sign of
"cracker bread" effect (that is, splashing of coat as
large droplets on the sheet surface) was present.
Obviously, due to the fully conformant deposition of the
coat layer applied by the spraying technique, the method
10 has some special characteristics and thus sets certain
requirements for the coating process. Accordingly, the
base sheet should have a maximally smooth surface.

15 The operating life of nozzles could not be evaluated
within the time span of tests performed. Experiences fr m
similar nozzles used in painting technology indicate that
the nozzle life will be rather limited, because abrasive
wear of the nozzle causes progressive narrowing of the
spray angle and widening of the nozzle orifice, whereby
20 both the surface quality and coat profile will suffer.
Therefore, the service life of nozzles in the spraying of
coating mixes need to be assessed in detail.

Claims:

1. A method of coating a moving web of paper or paper-board, in which method

5

- the web to be coated is passed to a coater station, wherein a coat layer is applied to at least one surface of the web, and

10

- the web is dried at least to some degree and passed to the next treatment step,

c h a r a c t e r i z e d i n t h a t

15

- the coat is applied by spraying the coating mix on the web surface by means of high-pressure spraying nozzles, whereby the pattern width covered by a single nozzle is essentially narrower than the cross-machine width of the web being coated.

20

2. A method as defined in claim 1, c h a r a c t e r i z e d i n t h a t the web being coated is precalendered prior to coating.

25

3. A method as defined in any of foregoing claims, c h a r a c t e r i z e d i n t h a t the coat is sprayed on any side of the web to be coated in at least two separate steps and the sprayed coat is dried between these steps.

30

4. A method as defined in any of foregoing claims, c h a r a c t e r i z e d i n t h a t the coat is sprayed on any side of the web to be coated in at least three separate steps and the sprayed coat is dried b t w e e n t h e s e s t p s.

35

5. A method as defined in any of foregoing claims,
c h a r a c t e r i z e d in that the coat is sprayed on
any side of the web to be coated in at least two separate
steps so that the successive coat layer is sprayed on the
5 still moist preceding layer.

6. A method as defined in any of claims 3 - 5,
c h a r a c t e r i z e d in that at least two differ nt
coat formulations are sprayed on the web.

10

7. A method as defined in claim 1, c h a r a c t e r -
i z e d in that a first coat layer is initially applied
to the web by means of a roll applicator, followed by
spray-coating of at least one successive coat layer onto
15 the still moist first layer by means of high-pressure
spraying nozzles.

8. A method as defined in claim 1, c h a r a c t e r -
i z e d in that a first coat layer is initially applied
20 to the web by means of a short-dwell applicator, followed
by spray-coating of at least one successive coat layer
onto the still moist first layer by means of high-
pressure spraying nozzles.

9. A method as defined in claim 1, c h a r a c t e r -
i z e d in that to the web surface are first applied two
coat layers on one coater station, followed by drying of
the web, and to the dried web is applied at least one
successive coat layer.

30

10. A method as defined in any of foregoing claims,
c h a r a c t e r i z e d in that to the surface of the
paper web being coated is appli d at least one coat layer
on the paper machine.

35

11. A method as defined in any of foregoing claims,
c h a r a c t e r i z e d in that to the paper web is

coated with in at least two coating steps and subjected to intermediate calendering prior to the subsequent application of next coat layer.

5 12. An arrangement for coating a moving web of paper or paperboard, said arrangement including

- means (1) for passing the web to be coated to a coater station (3), wherein a coat layer is
10 applied to at least one side of the web, and

- means (4, 5, 6) for drying the web at least to some degree and means (7) for passing the web to the next treatment step,
15

c h a r a c t e r i z e d b y

- at least one spray-coater (3) comprising at least one linear array of high-pressure
20 spraying nozzles, in which the pattern width on the web covered by a single spray is essentially narrower than the width of the web being coated.

25 12. An arrangement as defined in claim 11, c h a r - a c t e r i z e d by a precalender (2) located before the first spray-coater (3) in the machine direction of the moving web.

30 13. An arrangement as defined in claim 12, c h a r - a c t e r i z e d by comprising in the machine direction of the moving web the sequence of a precalender (2), a first spray-coater unit (3), at least one dryer (4, 5, 6), a second spray-coater unit (7), at least one dry r
35 (8, 9, 10) and a calender.

14. An arrangement as defined in claim 12, c h a r -
a c t e r i z e d by comprising in the machine direction
of the moving web the sequence of a precalender (2), a
first spray-coater unit (3), at least one dryer (4, 5,
5 6), a second spray-coater unit (7), at least one dryer
(8, 9, 10) and a winder (12) in combination with a
separate calender (13, 14).

15. An arrangement as defined in claim 12, said
10 arrangement being adapted to operate immediately in
conjunction with a paper machine (15), c h a r a c -
t e r i z e d by comprising in the machine direction of
the moving web the sequence of a precalender (2) suited
for treating the web passed from said paper machine (15),
15 a first spray-coater unit (16), at least one dryer (4, 5,
6), a second spray-coater unit (17), at least one dryer
(8, 9, 10), an intermediate calender (18), a third spray-
coater unit (19), at least one dryer (20, 21, 22), a
fourth spray-coater unit (23), at least one dryer (24,
20 25, 26), a calender (27) and a winder.

16. An arrangement as defined in claim 12, c h a r -
a c t e r i z e d by comprising in the machine direction
of the moving web the sequence of an unwinder (1), a
25 first spray-coater unit (3), at least one dryer (4, 5,
6), a second spray-coater unit (7), at least one dryer
(8, 9, 10), a third spray-coater unit (29), at least one
dryer (20, 21, 22), a fourth spray-coater unit (30), at
least one dryer (24, 25, 26), a winder (12) and at least
30 one separate calender (13, 14).

17. An arrangement as defined in claim 12, c h a r -
a c t e r i z e d by comprising in th machine direction
of the moving web the sequence of an unwinder (1), a pre-
35 calender (2), a first spray-coater unit (3), at least one
dryer (4, 5, 6), a second spray-coater unit (7), at least
one dryer (8, 9, 10), a first blade coat r unit (31), at

least one dryer (20, 21, 22), a second blade coater unit (32), at least one dryer (24, 25, 26) and a winder (12).

18. An arrangement as defined in claim 12, characterized by comprising in the machine direction of the moving web the sequence of an unwinder (1), a precalender (2), a first blade coater unit (33), at least one dryer (4, 5, 6), a second blade coater unit (34), at least one dryer (8, 9, 10), a first spray-coater unit (31), at least one dryer (20, 21, 22), a second spray-coater unit (32), at least one dryer (24, 25, 26) and a winder (12) in combination with at least one separate calender (13, 14).

19. An arrangement as defined in claim 12, characterized by comprising in the machine direction of the moving web the sequence of an unwinder (1), a precalender (2), a first transfer coater unit (35), at least one dryer (4, 5, 6), a second transfer coater unit (36), at least one dryer (8, 9, 10), an intermediate calender (18), a first spray-coater unit (29), at least one dryer (20, 21, 22), a second spray-coater unit (30), at least one dryer (24, 25, 26) and a winder (12) in combination with at least one separate calender (13, 14).

20. An arrangement as defined in claim 12, characterized by comprising in the machine direction of the moving web the sequence of an unwinder (1), a precalender (2), a first blade coater unit (33), at least one dryer (4, 5, 6), a second blade coater unit (34), at least one dryer (8, 9, 10), a first spray-coater unit (29), at least one dryer (20, 21, 22), a second spray-coater unit (30), at least one dryer (24, 25, 26) and a winder (12).

21. An arrangement as defined in any of claims 12 - 20, characterized by having its dryers comprised

of noncontacting dryers located after said coater units in-line so that the web path is continued essentially straight at the outgoing side of each coater unit.

- 5 22. An arrangement as defined in claim 21, c h a r -
a c t e r i z e d by including at least eight coater
stations.

1/7

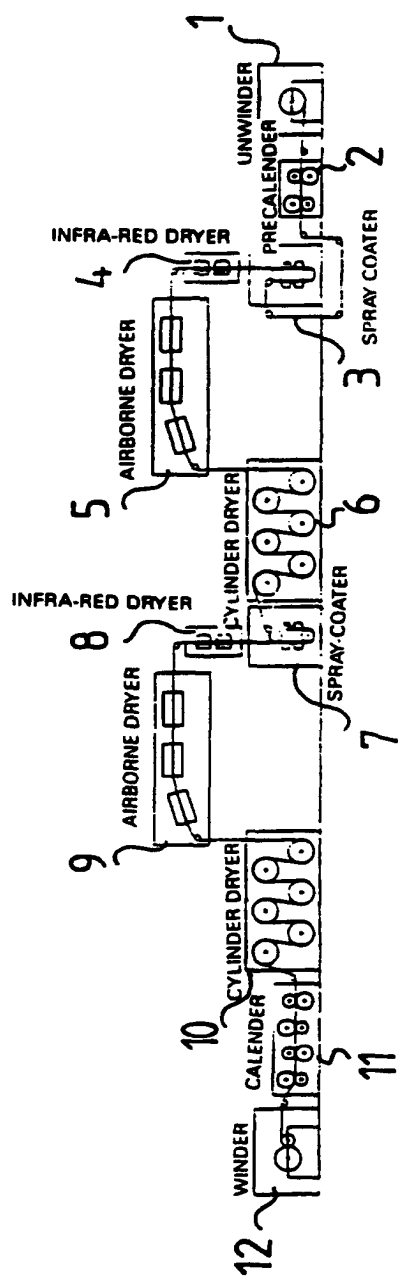


FIG. 1

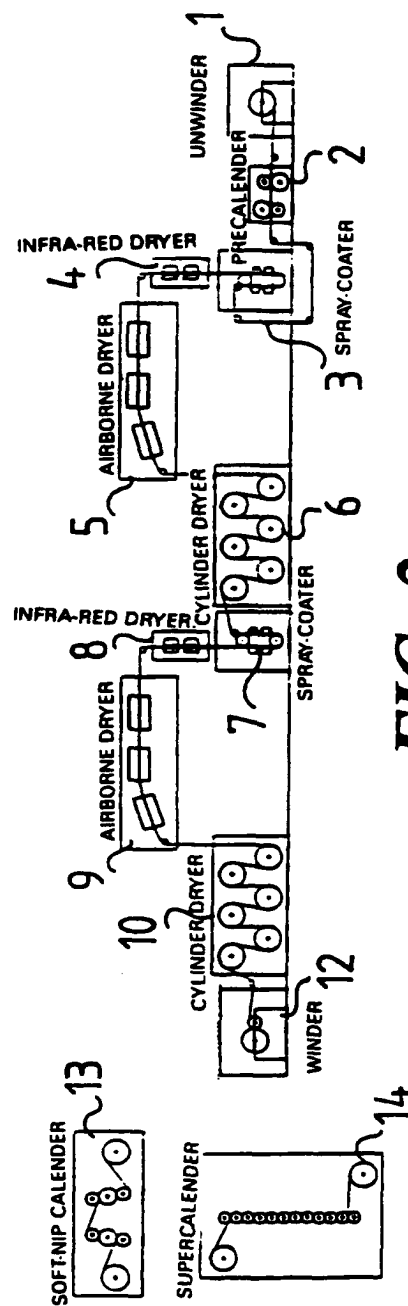


FIG. 2

2/7

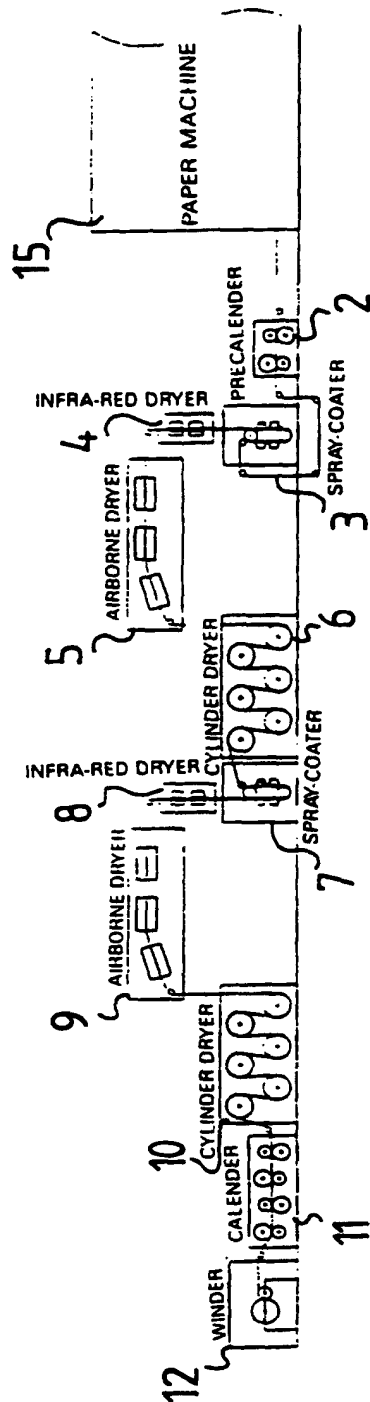


FIG. 3

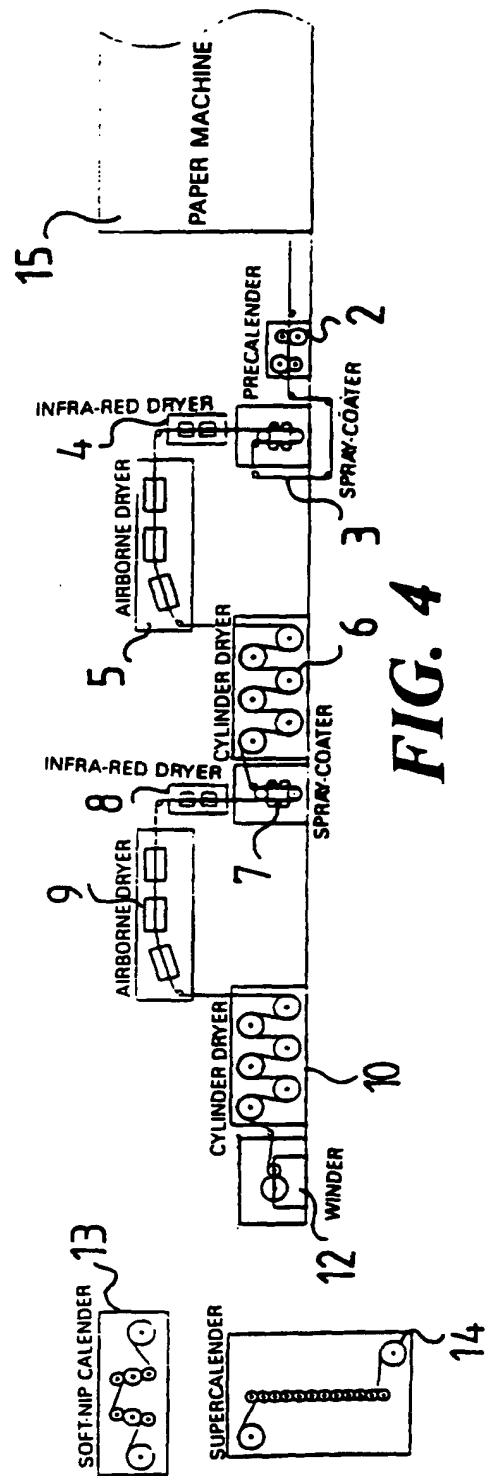


FIG. 4

3/7

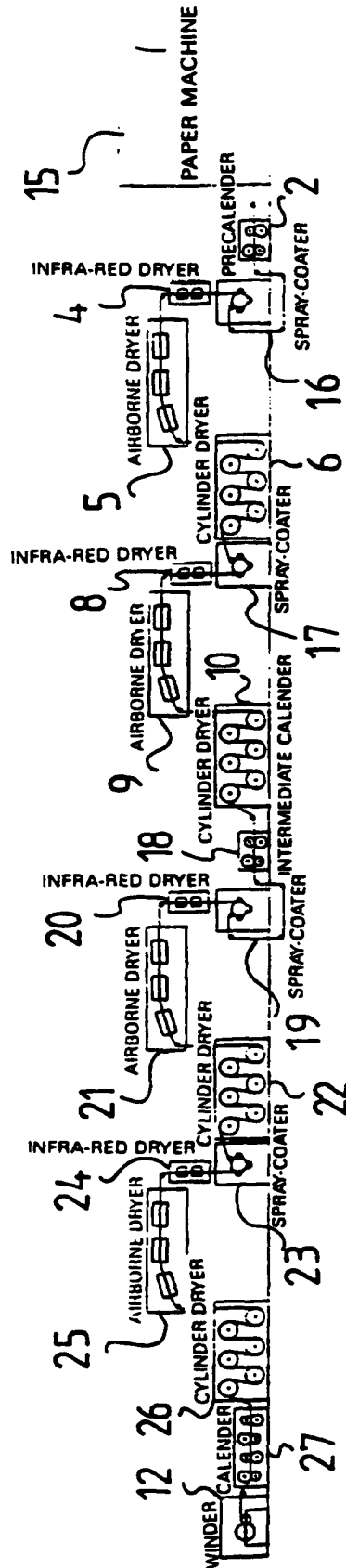


FIG. 5

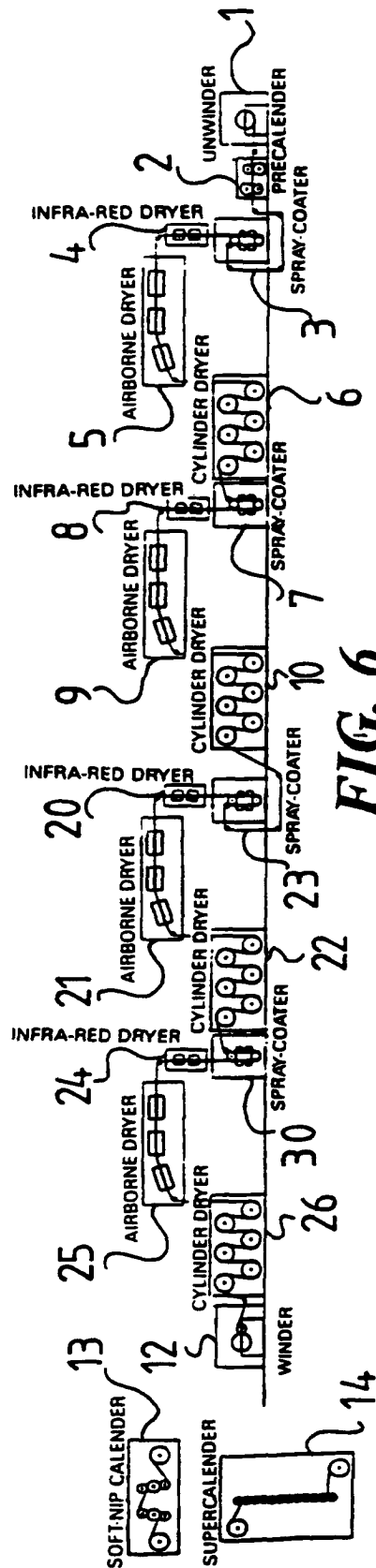
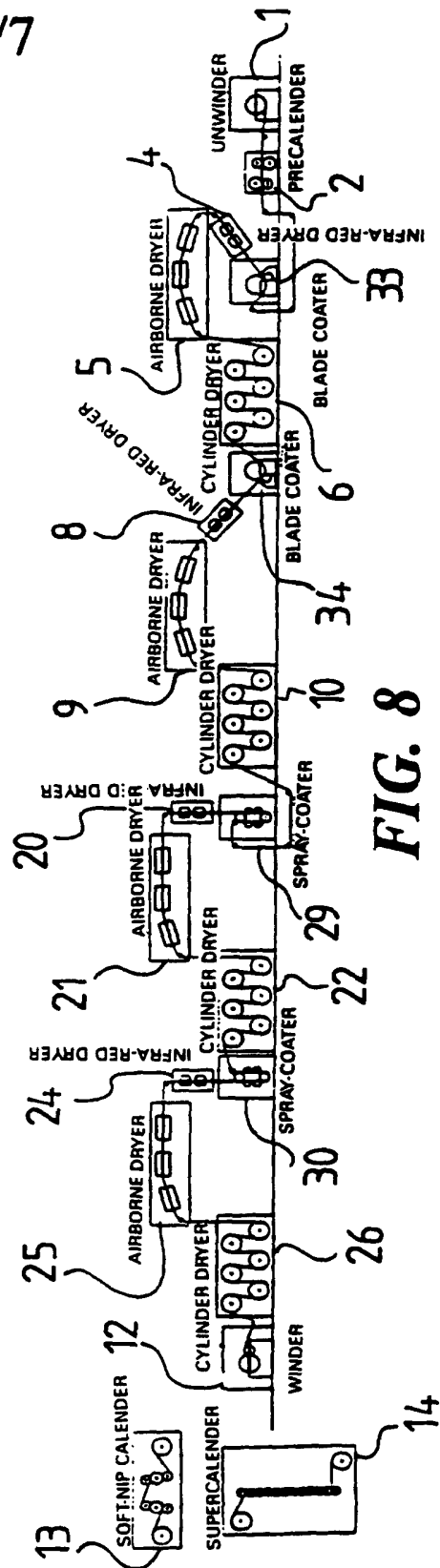
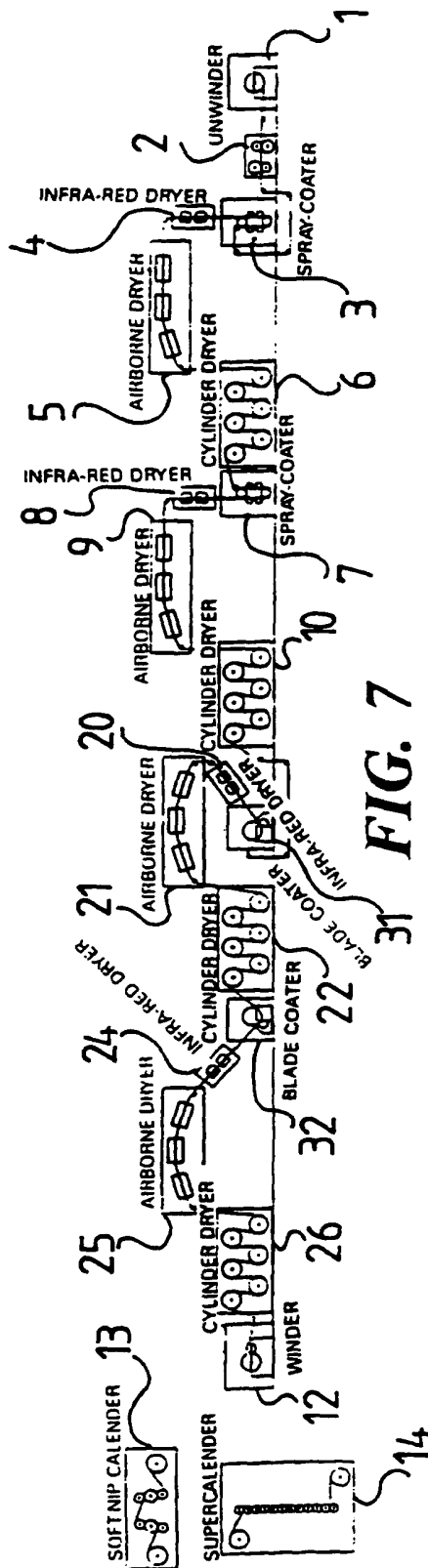
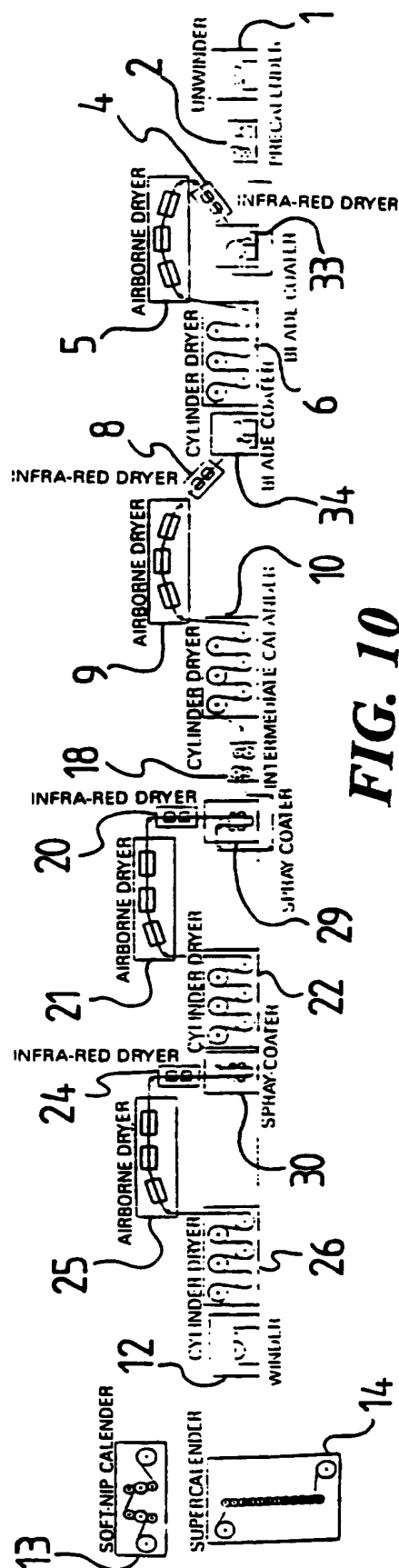
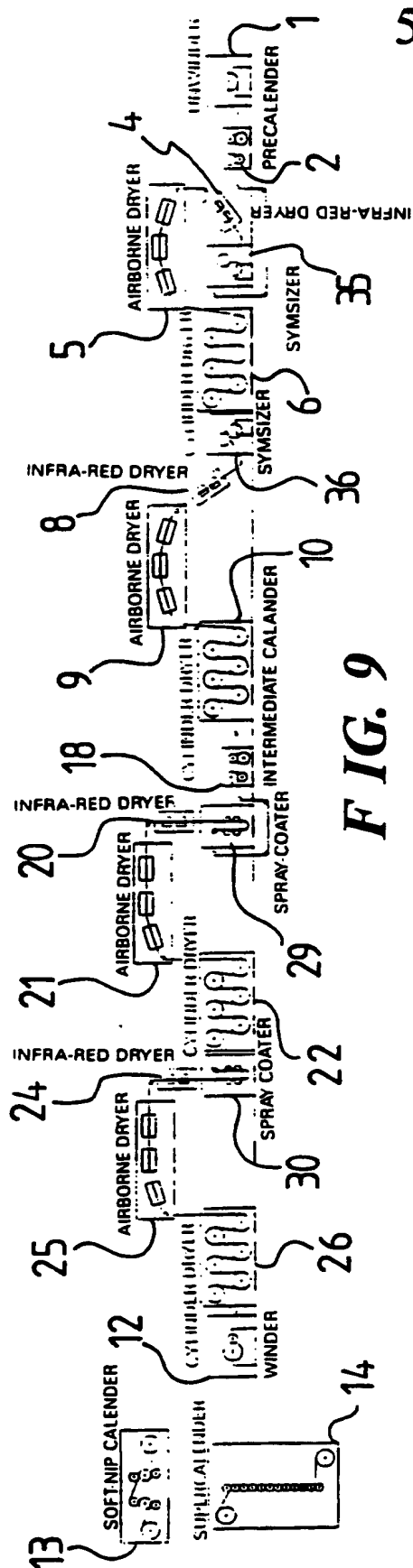
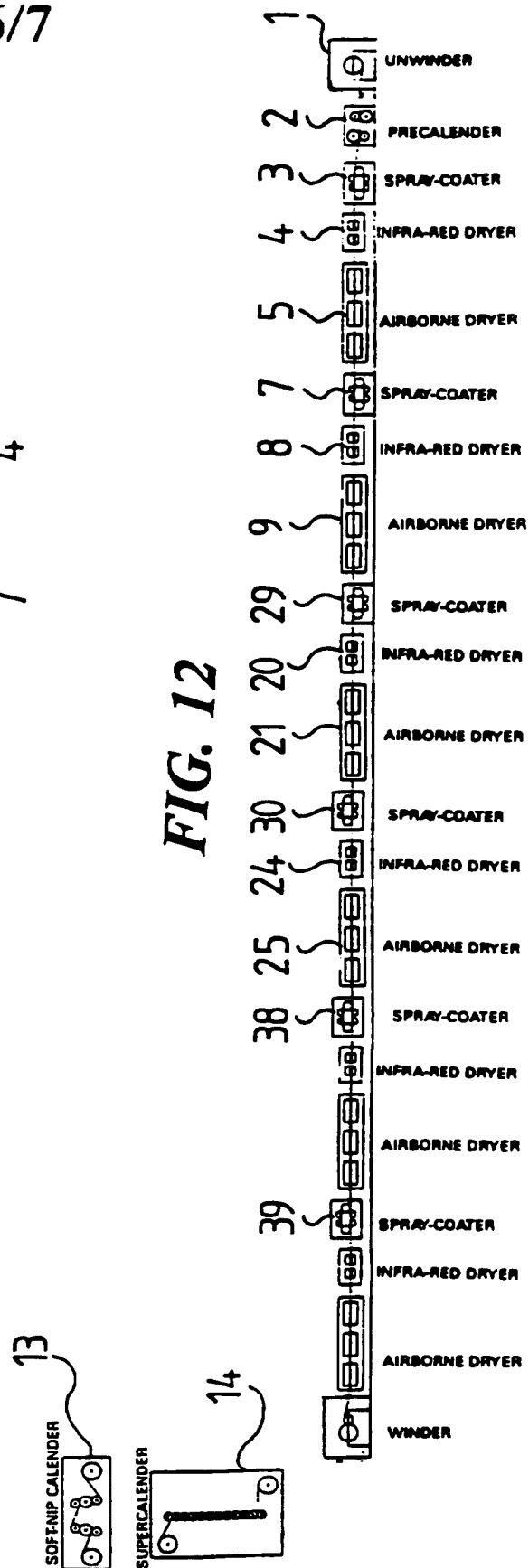
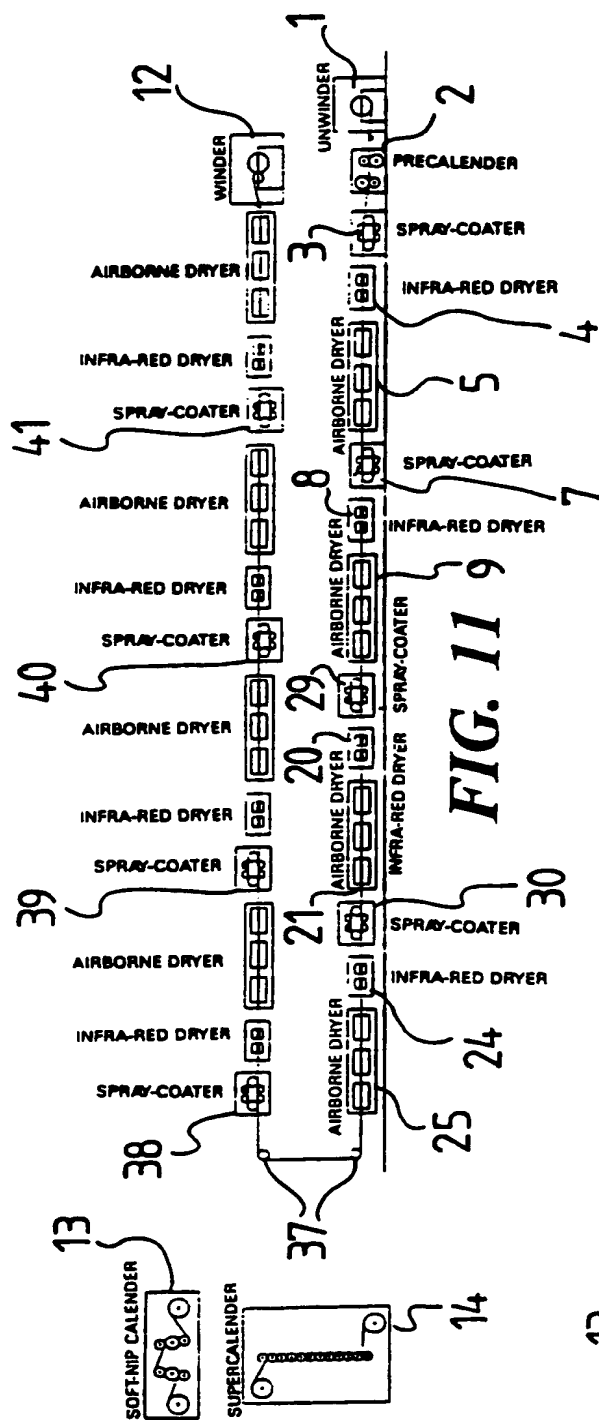


FIG. 6

4/7







7/7

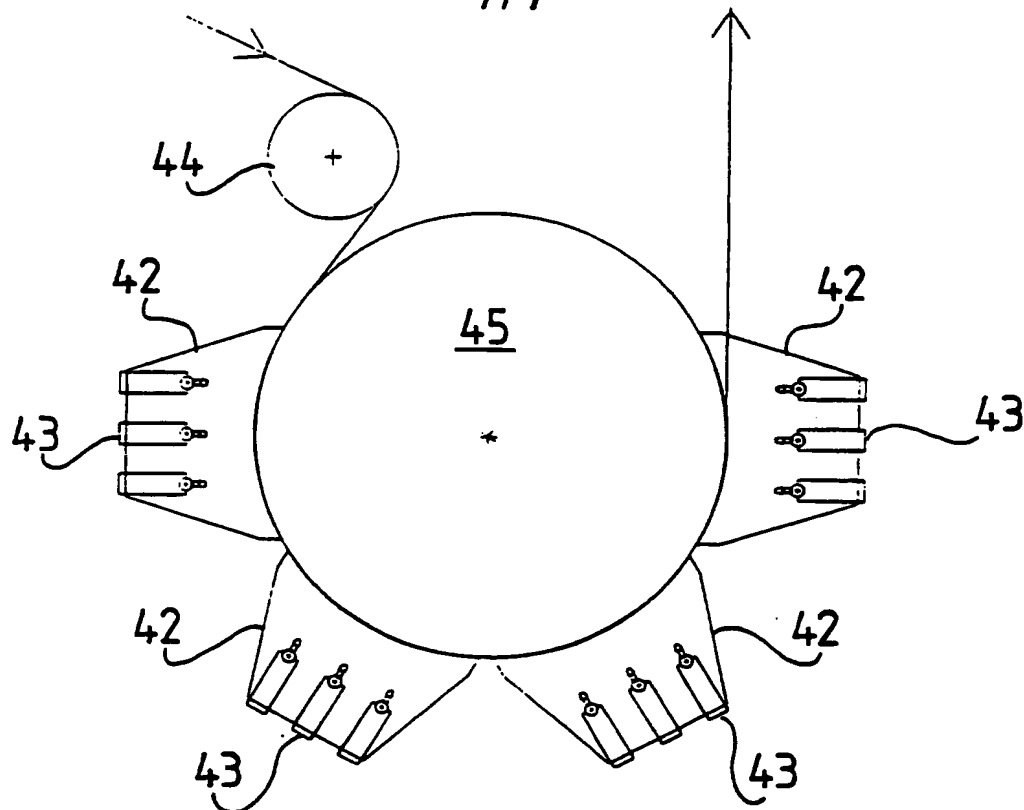


FIG. 13

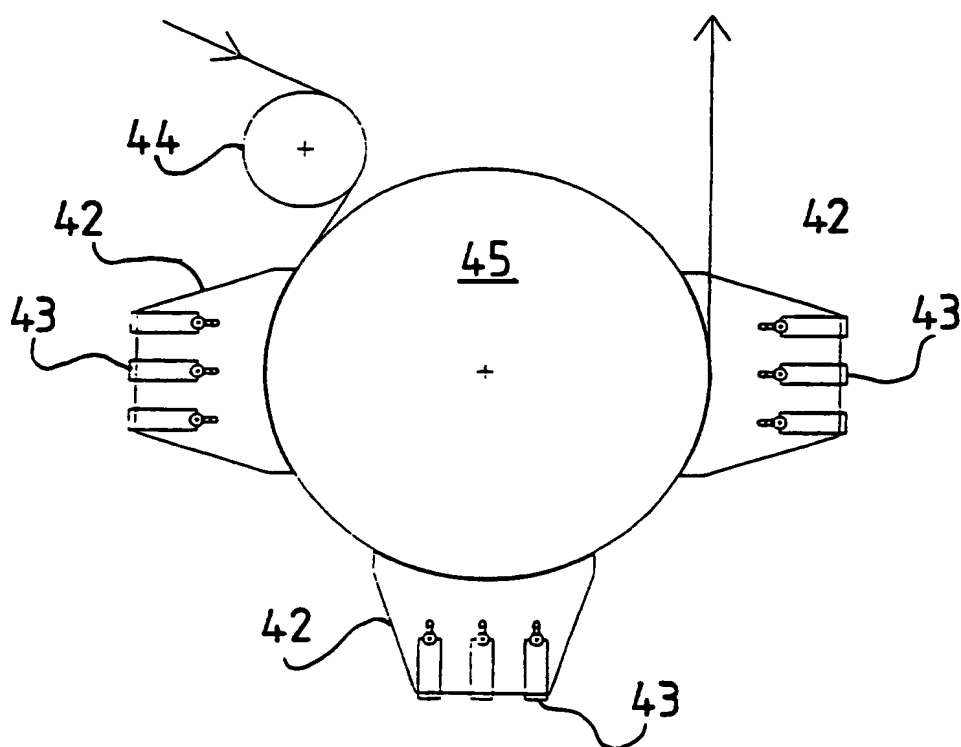


FIG. 14

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 96/00525

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21H 23/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	EP 0690171 A2 (VALMET PAPER MACHINERY INC.), 3 January 1996 (03.01.96), figure 1, abstract --	1-22
A	FI 81641 B (VALMET PAPER MACHINERY INC.), 31 July 1990 (31.07.90), claims --	1-22
A	WO 9411116 A1 (SUNDHOLM, PATRICK), 26 May 1994 (26.05.94), abstract -- -----	1-22



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

3 January 1997

Date of mailing of the international search report

18 -01- 1997

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Barbro Nilsson
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

28/10/96

International application No.

PCT/FI 96/00525

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0690171	03/01/96	CA-A- 2152645 FI-B- 97247 FI-A- 943191 JP-A- 8052398	02/01/96 31/07/96 02/01/96 27/02/96
FI-B- 81641	31/07/90	NONE	
WO-A1- 9411116	26/05/94	AU-A- 5421794 CA-A- 2148505 EP-A- 0682571 FI-B,C- 96894 FI-A- 925045 FI-A- 934890	08/06/94 26/05/94 22/11/95 31/05/96 07/05/94 07/05/94